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# Usefulness of Ethanol as a Quality Index of Fish and Fish Products - I

## The Relationship Between the Sensory Judgement of Canned Albacore and it's Ethanol Content.

Haruka IIDA, Toshio TOKUNAGA and Kooji NAKAMURA

Abstract: The canned products of fish for export are graded by sensory evoluation test. It is generally considered that flavour evaluation is the most important among many items judged in this test. But, there is little knowledge about the volatile components concerned with the flavour evaluation of caanned fish.

This study was carried out to clarify the kind of volatile components contributing to the flavour of canned fish. Namely volatile components of a high quality can graded as a—a' were compared with those of a low quality can evaluated as grade D.

When ethanol content was compared between the two grades of canned fish, it was found that the low grade can had 63 times more ethanol in the meat and 189 times more ethanol in the liquid, than in those of the high grade can. And there was little difference in analytical values of volatile components, except for ethanol, between the two grades.

From the results obtained, it was speculated that ethanol content of canned fish may be a useful index of the quality.

Quality evaluation of canned fisheries products destined for export is carried out mainly in a sensory fashion according to the export inspection standards of the Japanese Association for the Inspection of Canned Products. Among the numerous objects of inspection, color and flavor are most important. As it is closely related to the freshness of the materials employed, flavor quality is regarded to be very important. Skilled evaluators determine the flavor by holding a small amount of

sample in the mouth and by sniffing the same, and the precision of the determination results is said to be quite remarkable. Yet there has practically been no examination of the mode in which the volatile components contribute to this flavor determination. With the purpose of researching the substances which are at the basis of the sensory determination, we analyzed the volatile components of cans of different quality, and discovered great differences in the volumes of ethanol.

Recently, Lerke et al.[1]) proposed to measure the volumes of ethanol as an index of quality evaluation for canned tuna. In Japan one hardly hears of similar reports. As it also seems that in the future the volumes of ethanol in canned products for exportation may become a problem, we will report here on the results obtained so far.

## Samples and method

p. 78

### Samples

We used as samples boiled albacore cans of very different qualities which had been rated a - a' (excellent) and D (unfit for consumption) in a sensory fashion by inspectors of the Japanese Association for the Inspection of Canned Products. We show in Table 1 the storage conditions of the materials used for the sample cans inspected by the same association and the analysis results regarding the ATP-related substances in the canned meat. As the Table shows, the freshness of the materials used for the canned products rated a - a' for freshness was judged good and the measured values of the Hx ratio were around 10%. However, the freshness of the materials used for the canned products rated D dropped conspicuously, and the Hx ratio was nearing 40-50%.

Immediately after opening the can, the juice and solid matters were separated on a slanted surface and we analyzed them separately as follows.

Trapping of the volatile components and gas chromatography (GLC) analysis

To capture the volatile components, we followed the already reported method.[2] That is, we put 10 g of solid matters or 5 g of juice in the apparatus shown in Fig. 1, circulated synthetic air for 10 min at 50 mL per min over a 40°C warm bath and captured the volatilized components in a U-type tube immersed in liquid oxygen. Thereafter, we heated the U-type tube in about 1 min up to 120°C using a thermoinduction apparatus (Shimadzu FLS-1) and introduced the volatile components in a GLC apparatus for analysis.

The GLC conditions are as follows. Apparatus: Shimadzu, model GC-4CM; packing: Porapak QS; column: 1.5 m x 3 mm glass column; column temperature: 150°C; injection port temperature: 170°C; carrier gas: $N_2$ 30 mL/min; detector: FID; integrator: Shimadzu E-1A; chart speed: 10 mm/min.

Quantitative determination of histamine

We performed colorimetric determination by the method of Kawabata[3].

Quantitative determination of the volatile fatty acids

After acidifying with sulfuric acid the water vapor distillate trapped in the 1N-NaOH, we extracted repeatedly 8 times with ether[4]. We separated the ether through distillation at a temperature below 40°C, and washed the walls of the device with a small amount of methanol.

Then we performed GLC analysis after preparing determined volumes. The GLC conditions are as follows. Apparatus: Shimadzu GC-4CM; packing: 10% FALM/Shimalite TPA 60-80 mesh; column: 2 m x 3 mm glass column; p. 79
column temperature: 140°C; injection port temperature: 180°C; carrier gas: $N_2$ 30 mL/min; detector: FID.

Quantitative determination of dimethylamine nitrogen (DMA-N), trimethylamine nitrogen (TMA-N)

We performed the respective colorimetric assays by the dithiocarbamate method[5] with regard to DMA-N and by the picrate method[6] with regard to TMA-N.

## Results and discussion

### Gas chromatograms of the volatile substances

Fig. 2 shows the GLC charts of the hard matters and of the juices. We gave a No. to the main peaks. There appeared common peaks showing a good retention time (Rt) agreement between the solid matters and the juice in the A (excellent) and B cans (unfit for consumption). Table 2 shows the integrator counts of these peaks. An integrator count-based comparison of the quantitative relationships of the total volatile components of the cans A and B, shows with regard to the B cans 2.2 higher volumes for the solids and 2.5 higher volumes for the juices.

If we look at the contents, we find the greatest difference in the size of Rt 5.9 (peak No. 2), and this is the main cause for the differences in the total volumes of volatile components. That is, the proportions of peak No. 2 in the A cans with regard to the total is only 1.2% for the solid matter and 0.7% for the juice but they increase to 35.3% and 55.9% respectively in the B cans. When comparing the counts

while excepting No. 2 from the main peaks No. 1 - No. 7, we see that the B cans/A cans ratio is 1.3 for the solid matters, and 1.1 for the juice and that the B cans are only slightly above the A cans. This seems to suggest that the difference in the sensory evaluations of cans A,B is mainly due to the quantitative differences of peak No. 2.

Identification of the substances in peak No. 2

As it thus seems that the difference in flavor between the cans A and B could come from the differnce in the contents of the peak No. 2 substances, we attempted to identify these substances. That is, we introduced the volatile compounds trapped just as in the GLC analysis in a gas chromatography mass analyzer (Shimadzu model GC-MS, 7000) and performed the analysis. As a result, both the Rt and mass spectra in the GC-MS of these components agreed with ethyl alcohol so that the substance in peak No. 2 was identified as ethanol.

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Other analytical results

Table 3 shows the quantitative results for the volatile fatty acids. The total acid volumes are higher in the B cans than in the A cans for both solid matters and juice. There were no conspicuous differences among the particular acids. However, as Kikuchi et al.[7] reported that a peculiar smell begins to be perceived when the total acid volume exceeds 25 mg in 100 g, we considered the 20-24 mg/100 g total acid volume in the bad B cans used in these tests and thought that the effect of acid upon flavor determination cannot at all be ignored. Since the threshold value of a n-butyric acid aqueous solution is 1/1000[9] when volatilized in about 1/6 [8] of acetic acid, air, so from the

p. 80

particular viewpoint of connection with the threshold value for the juice of the B cans, the presence of butyric acid cannot be ignored.

Table 4 shows the analytical results obtained with regard to histamine-containing amines. The analytical results are only about the hard matters of both the A and B cans. Yet it is shown that the volumes of histamine contents are large in the B cans. Recently, the volume of histamine was chosen as chemical quality index for canned fisheries products in the US. If the concentration in the cans exceeds 25 mg/ p. 81
100 g, it is estimated that unsuited materials were used. The volume was not that high in the bad B cans used in the present tests. The probable reason is that the temperature at which the materials were left standing was relatively low. As for the relationship between the volume of histamine production and temperature, Takagi et al.[10] reported that there is a great difference in production volume at standing temperatures of 15°C and 25°C. For instance, when yellowtail materials are left standing at 19°C for 96 hours, the volume of histamine is 0.6 mg/100 g but when the temperature is 25°C and the time 48 h the volume is 153.8 mg/100 g.

As for the other amines, there is virtually no differnce between the cans A and B. The contents are relatively low and there seems to be no effect upon the flavor. However, the low proportion of DMA-N[11] with regard to TMA-N in the B cans indicated a difference in material freshness.

We thus estimated from the results of the present tests that the differences in sensory rating with regard to the flavor of the good A cans and bad B cans were caused mainly by differences in the volumes of ethanol production, and partly by differences in the volume of acids such as butyric acid.

Some causes have been suggested as for the production of ethanol during the freshness deterioration process. For instance, Lerk et al.[1]) point to a production from the glucoses caused by glucolytic action and to a production from alanine caused by bacterial action. We might also consider a production caused by acetoaldehyde reduction.

The results of our tests demonstrated that even in the case of fish heated as in canning, it is possible to ascertain from the amount of ethanol produced whether or not the original materials were fresh. Consequently, it seems appropriate to use the amount of ethanol produced during processing in hot-packed foodstuff products like cans as a chemical quality index. Yet, in order to actually use ethanol as an index for raw material freshness or for processed product quality, one should also study thoroughly the causes of its production, the correlation with freshness, the differences between the fish species and the volume variations during the processsing course.

At the end, I wish to thank the Japanese Association for the Inspection of Canned Products which donated the test samples.

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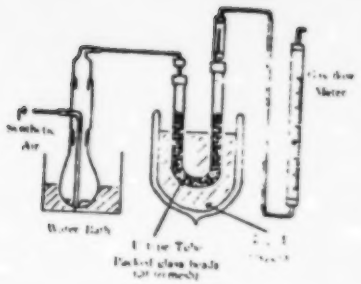

Fig. 1. The equipment used for trapping of volatile components.

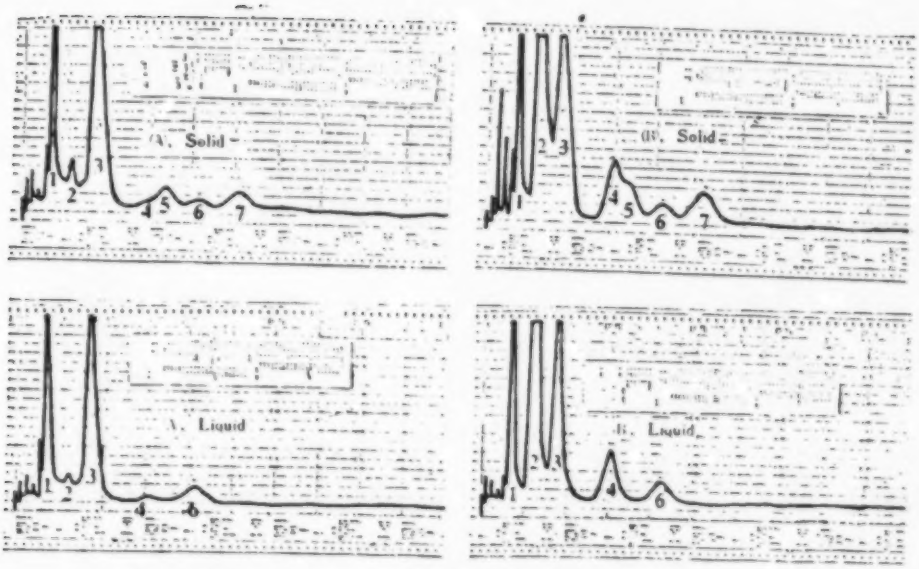


Fig. 2. The Gas-chromatograms of volatile materials in canned albacore
(A): Good quality can (B): Bad quality can

Table 1. Details of canned albacore used for analysis.

| | Storage Condition before canning | ATP breakdowns | | | Judgement* by odor |
|---|---|---|---|---|---|
| | | Hx (%) | HxR (%) | IMP (%) | |
| (A)** | 5 hrs, 19.0 °C | 10.1<br>12.5 | 49.5<br>50.0 | 40.4<br>37.5 | a—a' |
| (B)** | 143 hrs 18.5 °C | 51.8<br>47.3 | 43.7<br>49.8 | 4.5<br>2.9 | D |

* Judgement was carried out by inspection standard for canned tuna to be exported.
** (A): Good quality can (B): Bad quality can
These data were offered by the Japan Canned Food Inspection Association.

Table 2. Composition of volatile components in canned albacore

integrator counts ( $\times 10^4$ )

| Sample* / Peak No.* | (A) Solid | (B) Solid | (A) Liquid | (B) Liquid |
|---|---|---|---|---|
| 1 | 157 (27.7) | 198 (15.8) | 147 (35.9) | 130 (12.8) |
| 2 | 7 ( 1.2) | 441 (35.3) | 3 ( 0.7) | 366 (35.9) |
| 3 | 218 (38.5) | 239 (19.1) | 181 (44.1) | 158 (15.6) |
| 4 | 54 ( 9.5) | 129 (10.1) | 4 ( 1.0) | 69 ( 6.8) |
| 5 | | | — | — |
| 6 | 26 ( 4.6) | 41 ( 3.3) | 36 ( 8.8) | 41 ( 4.0) |
| 7 | 47 ( 8.3) | 74 ( 5.9) | — | — |
| Other Peaks | 57 (10.1) | 137 (10.6) | 39 ( 9.5) | 49 ( 4.8) |
| Total | 566 | 1,231 | 410 | 1,013 |

*: see Fig. 2 (%)

Table 3. Volatile acid contents in good (A) and bad (B) quality canned albacore. (mg/100 g sample)

| | (A) solid | (B) solid | (A) liquid | (B) liquid |
|---|---|---|---|---|
| Acetic acid | 6.9 | 16.9 | 10.9 | 11.4 |
| Propionic acid | trace | 2.3 | 1.1 | 0.6 |
| iso-Butyric acid | trace | trace | trace | trace |
| n-Butyric acid | 2.8 | 2.4 | 2.1 | 6.3 |
| iso-Valeric acid | 2.5 | 0.9 | 1.0 | 2.0 |
| n-Valeric acid | — | — | trace | — |
| iso-Caproic acid | trace | 0.5 | 0.8 | — |
| n-Caproic acid | 0.4 | 0.8 | 0.7 | — |
| Total | 12.5 | 23.7 | 16.6 | 20.3 |

Table 4. Contents of histamine and volatile amines in good (A) and bad (B) quality canned albacore.

| | Histamine* | DMA-N* | TMA-N* | DMA-N/TMA-N × 100** |
|---|---|---|---|---|
| (A) | 1.03 | 0.95 | 2.12 | 44.8% |
| (B) | 5.08 | 0.46 | 1.85 | 24.8% |

*: mg/100 g solid

**: The higher ratio indicates the better quality of can.

DMA-N: dimethylamine-N TMA-N: trimethylamine-N

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